Abstract No. dinn222

The Crystal Structure of the Cluster Compound $Nb_{22}Cl_{32}O_{13}$ from High Energy and High Resolution Powder Diffraction Data

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Beamline: X17B2

Introduction: Since the discovery of the $ScNb_6Cl_{13}O_3$ oxychloride (first oxyhalide containing Nb_6 octahedral clusters), numerous other cluster compounds have been isolated in the Nb-Cl-O system. All of them are characterised by Nb_6L_{18} units (L = Cl, O) that can be discrete or interconnected by shared ligands. During this investigation, a secondary phase was frequently detected in the X-ray powder diffraction patterns. After SEM observations and EDS analysis, it has been identified as a niobium oxychloride. Due to the fibrous character of this compound, high quality single crystals for a structural determination have not been obtained. However, a data collection on fibrous needles, performed on a CCD single crystal X-ray diffractometer, has allowed obtaining crude but reasonable structural models. The aim of a data collection on a high resolution synchrotron diffractometer is to determine a non ambiguous structural model for this phase. Due to strong preferred orientation effects, transmission mode was selected as the method of choice.

Methods and Materials: Data have been recorded at the high energy Beamline X17B2, in a capillary setup using a short wavelength (λ=0.1848 Å) in order to decrease absorption, minimize preferred orientation phenomena and to explore a large domain in reciprocal space (d_{min} ~ 0.9 Å).

Results: Preliminary results show that two different models can be considered. They are both characterized by a monoclinic unit cell (model I: P2/n with *a* = 15.556(1), *b* = 6.525(1), *c* = 12.882(1) Å, and *β* = 103.90(1)°; model II: C2/m with *a* = 31.107(2), *b* = 6.524(1), *c* = 12.881(1) Å, and *β* = 103.89(1) °). Both models are based on $Nb_6Cl_6^iO^i{}_6Cl^a{}_6$ units (Fig. 1 left) interconnected in one direction by sharing two inner oxygens and four apical chlorines, leading to infinite chains of unit. Additional niobium and chlorine atoms form two infinite $-Cl_2$-Nb-Cl_2-Nb- chains, linked to each other by additional oxygen atoms. The latter ones are bonded to the chains of units to form a layer (Fig. 1 right) by the remaining apical chlorine and inner oxygen ligands. The second model differs from the first one by an additional type of layer formed by edge-sharing clusters. The cohesion of both structures is assumed by van Der Waals interactions between the layers. The data analysis is still in progress. The crystal structure was refined by the GSAS Rietveld refinement package.

Acknowledgments: This work was supported by the Max-Planck-Society (MPG), the Fonds der chemischen Industrie (FCI) and the Division of Basic Energy Sciences, U.S. DOE (DE-FG02-86ER45231).

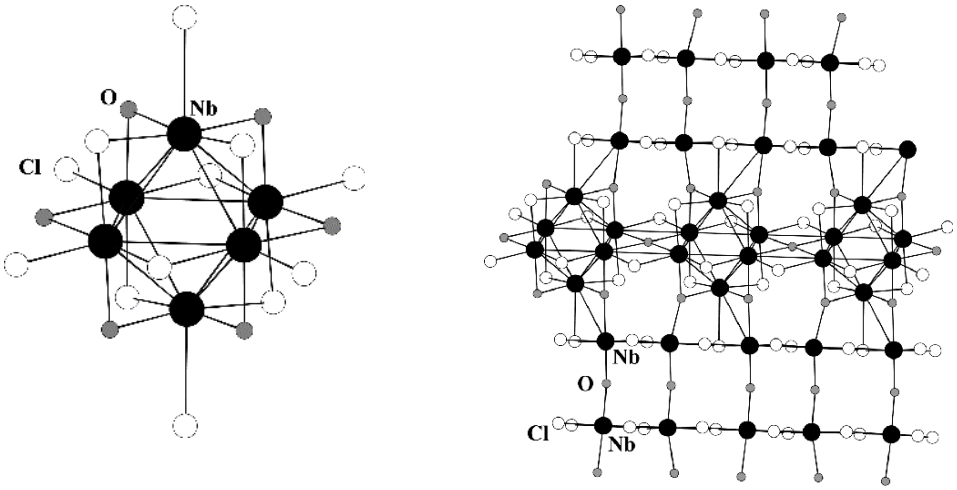

Figure 1. *Left* : $Nb_6Cl_6^iO^i{}_6Cl^a{}_6$ unit; *Right*: representation of the common layer in model I and II